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Distribution, speciation and geochemistry of selenium in contaminated marine sediments - Port Kembla Harbour, NSW, Australia

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DISTRIBUTION, SPECIATION AND GEOCHEMISTRY OF SELENIUM IN CONTAMINATED MARINE SEDIMENTS - PORT KEMBLA HARBOUR, NSW, AUSTRALIA

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Certification

I, Pattanan Tarin, declare that this thesis, submitted in fulfillment of the requirements for the award of Doctor of Philosophy, in the School of Earth and Environmental Sciences, University of Wollongong, is my own work unless otherwise referenced or acknowledged. The thesis has not been submitted for a degree at this or any other academic institution.

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Abstract

Selenium (Se) is an element of concern in Port Kembla Harbour as it was the only element found in harbour fish tissues in the mid-1990s at concentrations that exceeded the Australia New Zealand Food Authority Maximum Residue Limit. This thesis investigated the distribution, speciation, binding phases and geochemical behaviour of selenium in Port Kembla Harbour sediments, which potentially receive selenium pollution from local metal processing and smelting and coal industries. Sedimentary selenium is a potential selenium source for fish and organisms via benthic food chain transfer.

Grab surface sediments from 23 sites around the harbour and a total of 14 sediment cores were collected from the contaminated Red Beach area (during 2003-2006) and analysed for selenium concentrations by HG-AAS and also for sediment parameters including grain size composition, pH, redox potential, other trace metals, porewater composition and sediment macrocomponents. Two sequential extraction procedures were used to fractionate the solid-phase selenium into soluble and adsorbed, carbonate, metal oxyhydroxide, organically bound, elemental, organic matter and sulfide, and residual selenium fractions. The selenium behaviour in the different geochemical phases was examined in association with the measured sediment parameters.

The selenium concentrations in surface sediments from most harbour sites were low (below 3 μg/g) except those in sediments from the Red Beach area (up to 9.38 μg/g), which is in close proximity to a local copper refinery. Selenium concentrations in the Red Beach sediment cores ranged from 6 to 1735 μg/g, depending on depth and grain size, with peak selenium concentrations observed at 6-10 cm and at 14-16 cm depths. The highest selenium concentration (1735 μg/g), found in the <63 μm Red Beach sediments, was 100 times higher than the highest sedimentary selenium concentration previously reported in Australia. The sedimentary selenium was concentrated in fine (<63 μm) grains that are easily mobile. Selenium was correlated mainly with Pb, Cu and Zn in the > 250 μm fraction of the surface sediments and in the < 63 μm fraction of the sediment cores, indicating association from both original ore sources and through post-depositional transformation. The sediment ^{210}Pb dating estimated the sedimentation rate of Red Beach cores to be 0.55 ±

0.03 cm/year. Sediment ^{210}Pb dating provided an indication that the deeper sediments were not disturbed and high selenium concentrations in the sediment cores were a result of historical selenium input potentially from a copper smelter.

The solid-phase selenium in the Red Beach sediment cores was present mainly as elemental selenium. High proportions of the selenium were also bound to the organic matter in the upper 10 cm region and associated with the residual fraction below 10 cm. Selenite was the major selenium species found in the organically bound selenium fraction. Small proportions of the solid-phase selenium were in soluble and adsorbed fractions, with peak concentrations in the below 10 cm depth region. Minimal amounts of selenium were found to associate with iron-manganese oxyhydroxides and carbonate minerals in the sediment.

The Red Beach sediment cores were oxic in the top 2 cm and anoxic below 2 cm depths. The top 2 cm oxic sediment contained low solid-phase selenium concentrations and low porewater selenium concentrations. The anoxic 2-10 cm core region contained the peak solid-phase selenium concentrations but with low porewater selenium concentrations. This layer was enriched with the organic matter, AVS, organically bound selenium, and elemental selenium species, indicating a strong link between organic matter decay processes and the reduction of sulfate and selenium. The below 10 cm-anoxic sediments contained moderate solid-phase selenium, peak porewater selenium and high soluble and adsorbed selenium concentrations, and stable pyritic sulfur species. Selenium was observed to become associated with the residual fraction at the expense of the organically bound and the elemental selenium in this region. This below 10 cm region contained lower proportions of copper, lead and zinc in the residual fraction but significant amounts in the organically bound fractions. The solid-phase selenium correlated with the solid-phase sulfur through the association of their reduced forms: elemental selenium, pyrite and possibly as pyritic selenium. Copper was the only major element that co-extracted with elemental selenium. The reduced selenium forms (elemental and residual) correlated significantly with Cu, Pb and Zn, suggesting possible formation of independent CuSe, PbSe and ZnSe minerals in the sediment. Redox potential, sedimentation rate, organic matter components, sulfur and transition elements are concluded to be the important factors affecting the selenium geochemical behaviour in Red Beach cores.

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Abbreviations

μg	Microgram
μL	Microlitre
ANSTO	Australian Nuclear Science and Technology Organization
AVS	Acid Volatile Sulfide
BCR	Community Bureau of Reference
BDL	Below Detection Limit
CrRS	Chromium Reducible Sulfide
dMedSe	Dimethyldiselenide
dMeSe	Dimethylselenide
Eh	Redox potential
GF-AAS	Graphite Furnace-Atomic Absorption Spectrometry
HG-AAS	Hydride Generation-Atomic Absorption Spectrometry
HPLC	High Performance Liquid Chromatography
hr	Hour
HS	Humic substance
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
KOAc	Potassium Acetate
kPa	Kilopascal
K_{sp}	Solubility product
LOD	Limit of Detection
MeOH	Methanol
mV	Millivolt
NA	Not analysed
NaOAc	Sodium Acetate
ND	Not Detected
NIST	National Institute of Standards and Technology
NRCC	National Research Council of Canada
NS	No sample
pK_a	Log acid dissociation constant

PKC	Port Kembla Copper Limited
PKPC	Port Kembla Port Corporation
PW	Porewater
PZC	Point of Zero Charge
RNAA	Radiochemical Neutron Activation Analysis
RPC	Reversed Phase Chromatography
RSD	Relative Standard Deviation
SAX	Strong Anion Exchange
SE	Standard Error
SeCys	Selenocysteine
$SeCys_2$	Selenocystine
SeCyst	Selenocystamine
SeEt	Selenoethionine
Se^{IV}	Selenite
SeMet	Selenomethionine
SEP	Sequential Extraction Procedure
SeU	Selenourea
Se^{VI}	Selenate
TC	Total Carbon
TFE	Tetrafluoroethylene
TMAH	Tetramethylammonium hydroxide
TMeSe	Trimethylselenonium
TN	Total Nitrogen
TOC	Total Organic Carbon
TS	Total Sulfur
UC	University of Canberra
XAS	X-Ray Absorption Spectrometry
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence Spectrometry